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Supporting Information

Use of Supramolecular Assemblies as Lithographic Resists

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SUPPORTING INFORMATION:

Experimental Section

Compounds **1** - **5** were made as described in references 17, 19 – 21 of the main text. We describe film fabrication for **1**; the films of **2** – **5** were spun in the same manner.

Film fabrication.

The fabrication process is as follows: for films with a thickness of 60 and 30 nm, compound **1** (15 mg) was dissolved in 2.0 and 5.5 g of *t*-butylmethylether, respectively. The solutions were filtered using 0.2 μm PTFE syringe filters. The resists were then spun onto 10 mm × 10 mm silicon substrates using a spin cycle of 8000 rpm for 60 seconds, which was followed by a soft–bake at 100˚C for 2 minutes, allowing the cast solvent to evaporate. The resist films resulted with thicknesses of 60 and 30 nm, respectively.

The chemical integrity of each film was checked by X-ray photoelectron spectroscopy. Data were collected on a SPECS instrument equipped with a Phiobos 150 analyser and monochromated Al-Kα source (1486.6 eV). A flood gun was employed to compensate for charging of the sample. Compositions have been calculated using CASA XPS^{TM} sensitivity correction factors and corrected for with the analyser transmission function.

Table 1 gives the calculated elemental and experimental compositions for the molecule with ratios scaled to chlorine, the least abundant element present. The significant disagreement in the carbon composition is attributable to "adventitious carbon" that is deposited on the surface of the film. This contamination layer is always encountered for samples that have been exposed to air, and is associated with hydrocarbons present in the atmosphere. This extra layer of carbon on the surface has increased the percentage of carbon relative to the other elements and consequently decreased the expected composition for all the other elements. Smooth films were observed by atomic force microscopy (Figure S1).

Table S1. Elemental composition of deposited film as measured by XPS.

	Calculated Composition for **1** %	Calculate ratio's relative to Cl for **1**	Experimental Composition of film of **1**%	Ratio's relative to Cl of film of **1**
Carbon	61.5	51	69.1	74
Oxygen	23.8	20	19.7	21
Fluorine	4.9	4	3.84	4
Chromium	4.3	3.6	3.33	3.5
Nickel	1.8	1.5	1.41	1.5
Nitrogen	2.4	2	1.74	1.9

Chlorine	1.2	1	0.94	1

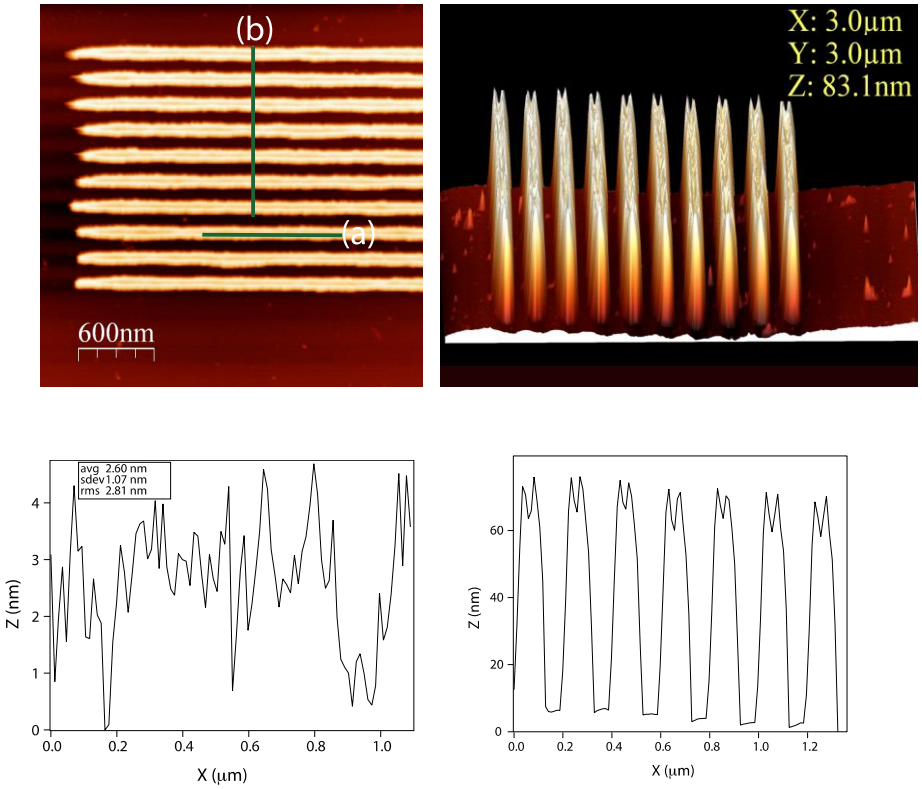

Figure S1: Atomic force microscopy of a film of **1** spun onto silicon from a *t*-butylmethylether solution and written to give 80 nm deep features. Panel bottom left shows a track along the top of a feature, path (a) in top left panel, with a surface roughness less than 4 nm while panel bottom right shows features 80 nm tall, path (b) in top left panel.

Experimental Lithography Conditions.

Two patterns were exposed; the first pattern consisted of a 1-dimensional matrix that had 200 single pixel lines separated by a pitch of 20 nm. The second pattern consisted of a 1-dimensional matrix that had 200 single pixel lines separated by a pitch of 200 nm; this pattern was used for the plasma etch experiments. Each single pixel line was assigned with an individual dose from 1 to 20.9 pC cm^{-1} in incremental steps of 0.1 pC cm^{-1}. All resists were then exposed using a FEI Sirion Scanning Electron Microscope (SEM), which had a RaithElphy plus 6MHz pattern generator attached to it. The exposed patterns were written using an acceleration voltage of 30 keV and a probe current of 50 pA; the dwell time was 8 μS and the step size was 4 nm. From these exposure parameters, the base dose was calculated to be 1000 pC cm^{-1}. Each pattern was exposed using a write field of 100 μm. Each material was developed using a solution of hexane, for 10 s followed by an N_2 blow dry.

Etch Conditions.

Etching studies used a Pseudo Bosch process that used an inductively coupled plasma (ICP) of SF_6 and C_4F_8 gases at 1200 W combined with a reactive ion etching (RIE) power of 20 W for 90 and 210 seconds.

X-ray Photoelectron Spectroscopy (XPS)

Compound **1** was spun coated on silicon where t-butylmethyl ether was the cast solvent and was exposed to the electron beam at an acceleration voltage of 30KeV. XPS studies were performed in order to understand the chemical and physical processes that occurred when the material was exposed to the electron beam. Table 1 gives the experimental compositions for the molecule with ratios scaled to chlorine, the least abundant element present.

Table S2: Elemental composition of unexposed and exposed material as measured by XPS.

	C 1s %	O 1s %	F 1s %	Cr 2p %	Ni 2p %	N 1s %	Cl 2p%
Before e-beam exposure	69.1	19.7	3.84	3.33	1.41	1.74	0.94
After e-beam exposure at 30KeV	65.2	21.8	3.1	4.2	2.3	1.9	1.6

Figure S2a illustrates that the electron beam exposure has changed the structure of Carbon 1s, the spectra shows a reduction in intensity at a binding energy of 288.5eV, this is due to the damage caused by the electron beam. When the incident electrons collide with the pivolates

they experience a scission, this results in a reduction in the carboxylate groups present. Thus making the molecule insoluble to the developer which is Hexane.

The Cr 2p spectra shows significant changes with the peaks showing both broadening and a shift to lower binding energies. The broadening is indicative of multi oxidation states existing in the Chromium with the shift to lower binding energies indicating reduction of the Cr towards Cr 0, which is insoluble in Hexane. Typically, Chromium $2p_{3/2}$ peak positions are Cr III oxide has a binding energy of ca. 576 eV, Cr IV oxide ca. 580 eV and Cr metal 574.4 eV.

The spectra of O 1s showed no change. The oxygen is bound to chromium which form small clusters of both Cr_xO_y and is insoluble in Hexane and provides the mechanism to a very high resistance to the etching process because the exposed molecule is not reactive in a SF_6 or C_4F_8 plasma. Hence, the dry etch rate is extremely low.

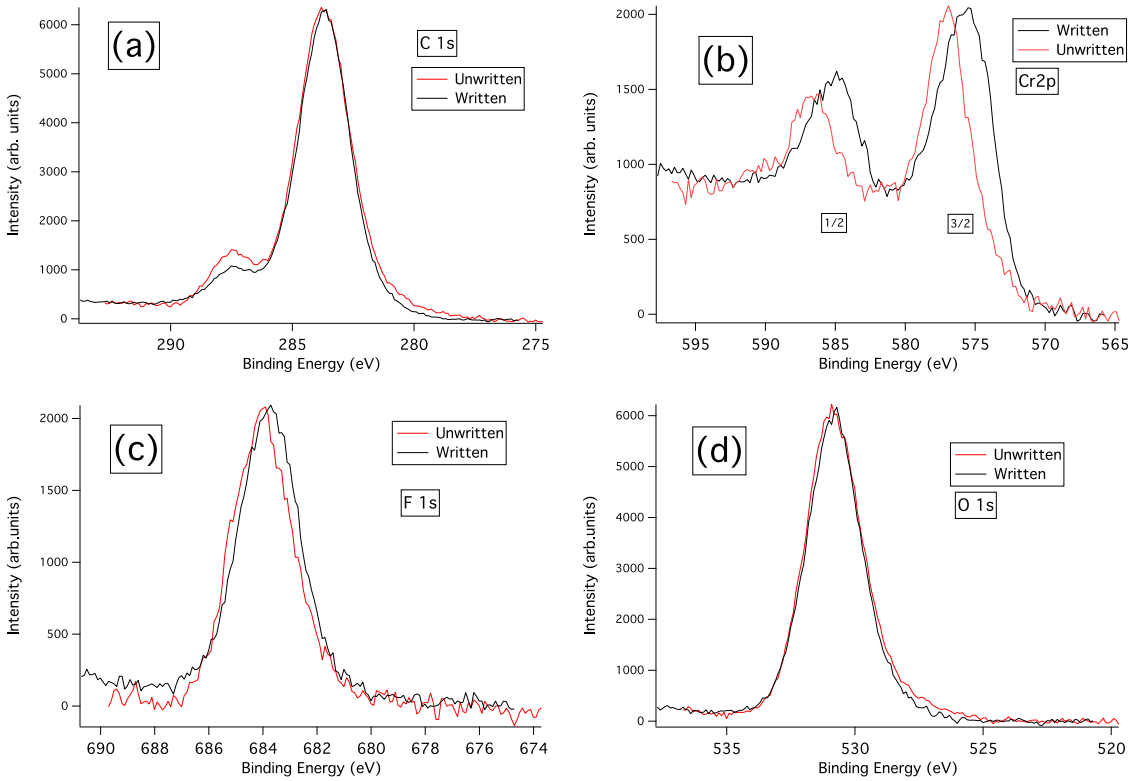

Figure S2: a) Photoelectron spectra of C 1s region from written and unwritten resist material, b) Photoelectron spectra of Cr 2p region from written and unwritten resist material, c) Photoelectron spectra of F 1s region from written and unwritten resist material, d) Photoelectron spectra of O 1s region from written and unwritten resist material.

Comparative Studies with Other Materials

Compounds **2** – **5** were deposited using very similar conditions. In Figure S3 we show images of these compounds and structures written into the resist using a 30 KeV SEM as described above.

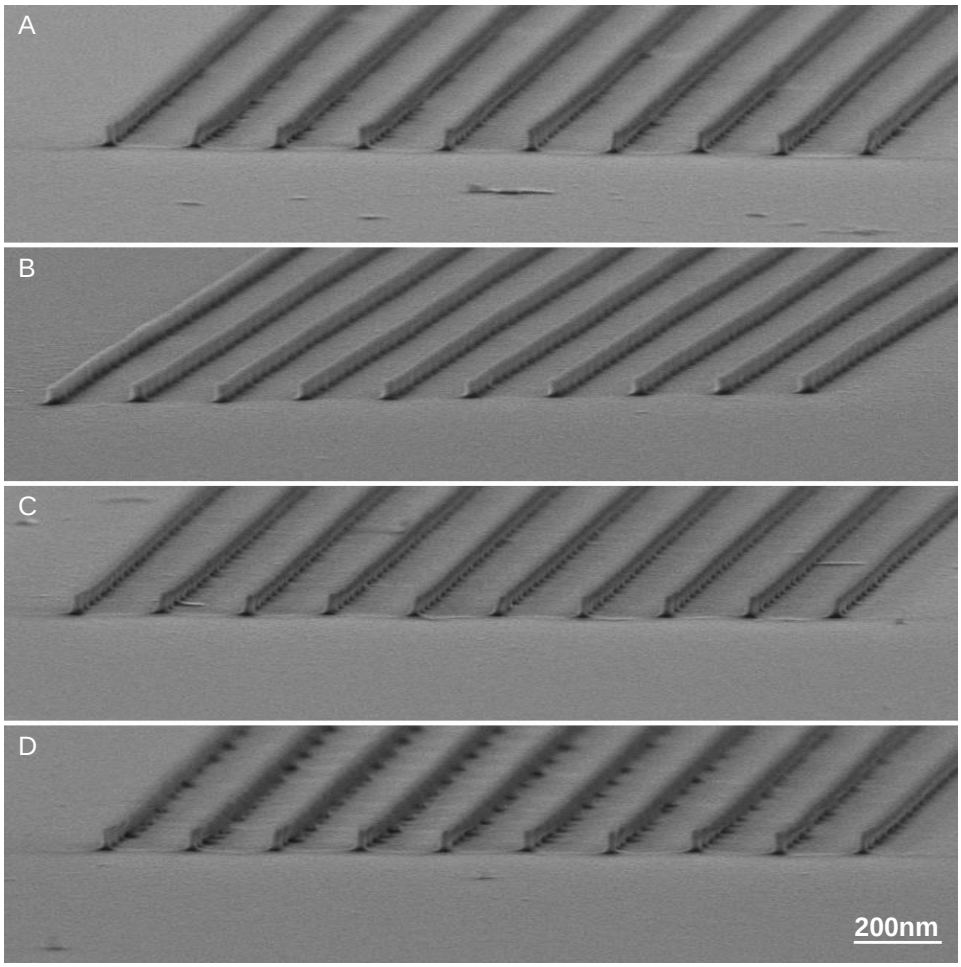

Figure S3: a) 12 nm lines on a 200 nm pitch written in **2**. b) 24 nm lines on a 200 nm pitch written in **3**. c) 10 nm lines on a 200 nm pitch written in **4**. d) 8 nm lines on a 200 nm pitch written in **5**.